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(54) **Reactive mesogenic azulenes**

(57) The invention relates to new reactive mesogenic azulene derivatives, their use as semiconductors or charge transport materials, in optical, electro-optical or electronic devices like for example liquid crystal displays, optical films, organic field effect transistors (FET or OFET) for thin film transistor liquid crystal displays

and integrated circuit devices such as RFID tags, electroluminescent devices in flat panel displays, and in photovoltaic and sensor devices, and to a field effect transistor, light emitting device or ID tag comprising the reactive mesogenic azulenes.

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DescriptionField of Invention

[0001] The invention relates to new reactive mesogenic azulene derivatives. The invention further relates to their use as semiconductors or charge transport materials, in optical, electro-optical or electronic devices like for example liquid crystal displays, optical films, organic field effect transistors (FET or OFET) for thin film transistor liquid crystal displays and integrated circuit devices such as RFID tags, electroluminescent devices in flat panel displays, and in photovoltaic and sensor devices. The invention further relates to a field effect transistor, light emitting device or ID tag comprising the reactive mesogenic azulenes.

Background and Prior Art

[0002] Organic materials have recently shown promise as the active layer in organic based thin film transistors and organic field effect transistors [see H. E. Katz, Z. Bao and S. L. Gilat, *Acc. Chem. Res.*, 2001, **34**, 5, 359]. Such devices have potential applications in smart cards, security tags and the switching element in flat panel displays. Organic materials are envisaged to have substantial cost advantages over their silicon analogues if they can be deposited from solution, as this enables a fast, large-area fabrication route.

[0003] The performance of the device is principally based upon the charge carrier mobility of the semi-conducting material and the current on/off ratio, so the ideal semiconductor should have a low conductivity in the off state, combined with a high charge carrier mobility ($> 1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). In addition, it is important that the semi-conducting material is relatively stable to oxidation i.e. it has a high ionisation potential, as oxidation leads to reduced device performance.

[0004] A known compound which has been shown to be an effective p-type semiconductor for OFETs is pentacene [see S. F. Nelson, Y. Y. Lin, D. J. Gundlach and T. N. Jackson, *Appl. Phys. Lett.*, 1998, **72**, 1854]. When deposited as a thin film by vacuum deposition, it was shown to have carrier mobilities in excess of $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with very high current on/off ratios greater than 10^6 . However, vacuum deposition is an expensive processing technique that is unsuitable for the fabrication of large-area films.

[0005] Regular poly(3-hexylthiophene) has been reported with charge carrier mobility between 1×10^{-5} and $4.5 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, but with a rather low current on/off ratio between 10 and 10^3 [see Z. Bao et al., *Appl. Phys. Lett.* 1997, **78**, 2184]. In general, poly(3-alkylthiophenes) show improved solubility and are able to be solution processed to fabricate large area films. However, poly(3-alkylthiophenes) have relatively low ionisation potentials and are susceptible to doping in air [see H. Sirringhaus et al., *Adv. Solid State Phys.* 1999, **39**, 101].

[0006] It was an aim of the present invention to provide new organic materials for use as semiconductors or charge transport materials, which are easy to synthesise, have high charge mobility and good processability. The materials should be easily processable to form thin and large-area films for use in semiconductor devices. Other aims of the invention are immediately evident to those skilled in the art from the following description.

[0007] It was found that the above aims can be achieved by providing reactive mesogenic azulene compounds, also referred to as reactive azulene mesogens, according to the present invention as described below. They consist of a central mesogenic core comprising one or more azulene groups, and optionally comprising further unsaturated organic groups that form a conjugated system together with the azulene groups, said mesogenic core being linked, optionally via a spacer group, to one or more polymerisable groups. The reactive mesogenic azulenes can induce or enhance liquid crystal phases or are liquid crystalline themselves. They can be oriented in their mesophase and the polymerisable group can be polymerised or crosslinked in situ to form polymer films with a high degree of order, thus yielding improved semiconductor materials with high stability and high charge carrier mobility.

[0008] Grell et al., *J. Korean Phys. Soc.* 2000, **36**(6), 331 suggest a reactive mesogen comprising a conjugated distyrylbenzene core with two reactive acrylate end groups as a model compound for molecular electronics. However, there is no disclosure of reactive mesogens of azulene.

[0009] Non-reactive, low molar mass azulene derivatives for use as components of liquid crystal compositions are shown for example in JP-A-02-069437, JP-A-02-069441 and JP-A-03-122189. The synthesis and polymerisation of an acrylate with an azulene group is described in Wada et al., *J. Polym. Sci., Polym. Chem. Ed.* 1978, **16**(8), 2085.

[0010] A further aspect of the invention relates to liquid crystal polymers, in particular liquid crystal side chain polymers obtained from the azulene reactive mesogens according to the present invention, which are then further processed e. g. from solution as thin layers for use in semiconductor devices.

Definition of Terms

[0011] The terms 'liquid crystalline or mesogenic material' or 'liquid crystalline or mesogenic compound' means materials or compounds comprising one or more rod-shaped, lath-shaped or disk-shaped mesogenic groups, i.e. groups

with the ability to induce liquid crystal phase behaviour. The compounds or materials comprising mesogenic groups do not necessarily have to exhibit a liquid crystal phase themselves. It is also possible that they show liquid crystal phase behaviour only in mixtures with other compounds, or when the mesogenic compounds or materials, or the mixtures thereof, are polymerised.

[0012] The term 'reactive group' or 'reactive compound' includes compounds or groups that are capable of participating in a polymerisation reaction, like radicalic or ionic chain polymerisation, polyaddition or polycondensation, as well as compounds or groups that are capable of being grafted for example by condensation or addition to a polymer backbone in a polymeranalogous reaction.

[0013] The term 'film' includes self-supporting, i.e. free-standing, films that show more or less pronounced mechanical stability and flexibility, as well as coatings or layers on a supporting substrate or between two substrates.

Summary of the Invention

[0014] One object of the invention are reactive mesogenic azulenenes, consisting of a central mesogenic core comprising one or more azulene groups, and optionally comprising further unsaturated organic groups that form a conjugated system together with the azulene groups, said mesogenic core being linked, optionally via spacer groups, to one or more reactive groups.

[0015] Another object of the invention is the use of reactive mesogenic azulenenes as semiconductors or charge transport materials, in particular in optical, electro-optical or electronic devices, like for example in field effect transistors as components of integrated circuitry, as thin film transistors in flat panel display applications or RFID tags, or in semiconducting components for organic light emitting diode (OLED) applications such as electroluminescent displays or backlights of flat panel displays, for photovoltaic or sensor devices, or as light-modulating components for liquid crystal displays, optical films or other optical or electrooptical devices.

[0016] Another object of the invention is a field effect transistor, for example as a component of integrated circuitry, as a thin film transistor in flat panel display applications, or in an RFID tag, comprising one or more reactive or polymerised mesogenic azulenenes according to the present invention.

[0017] Another object of the invention is a semi-conducting component, for example in OLED applications like electroluminescent displays or backlights of flat panel displays, in photovoltaic or sensor devices, comprising one or more reactive or polymerised mesogenic azulenenes according to the present invention.

Detailed Description of the Invention

[0018] The reactive azulenenes according to the present invention provide several advantages over prior art materials

- by adding substituent chains and other groups to the azulene core they can be made more soluble, thus being suitable for spin coating or solution coating techniques, rather than vacuum deposition, to prepare thin films for use e.g. in electronic devices such as transistors,
- they can be made mesogenic or liquid crystalline, thus exhibiting a higher degree of order that leads to particularly high charge carrier mobility, in particular when being aligned in their mesophase into macroscopically ordered orientation
- their macroscopic mesophase properties can be frozen in by in situ polymerisation,
- they combine the properties of a semi-conducting material with those of a mesogenic material to give novel materials with a rigid, planar conjugated core and a flexible chain to increase solubility and to decrease the melting point, which show high charge carrier mobility when being aligned in their mesophase.

[0019] The inventive reactive mesogenic azulenenes are useful as charge transport semiconductors, in that they have high carrier mobilities. In particular, the introduction of side groups to the conjugated rings bonded to the azulene core improves their solubility and therefore their solution processability. In the compounds according to the present invention, the azulene group is a mesogenic group or part of a mesogenic group. These compounds are therefore particularly useful as semiconductors or charge transport materials, as they can be processed while in the highly ordered mesophase morphology, and readily aligned by conventional techniques in a preferred direction. Both smectic and nematic mesophase ordering allows close packing of molecular pi-electron systems, which maximises intermolecular charge transfer which occurs through a hopping mechanism between adjacent molecules. This ordered, and oriented microstructure can be permanently "frozen-in" by polymerising the mesogens, which can also create a structure with long range order, or "monodomain". Formation of a monodomain also maximises charge transfer by eliminating charge trap

sites at grain boundaries, while the polymerisation also improves the mechanical properties of the film. Further, by cross-linking the mesogens, a highly stable structure results, which has an additional advantage of being impervious to subsequent processing solvents during device fabrication, thus allowing a wider range of solvents to be used in deposition of the next layer of the device by solution techniques. In addition, it is often observed that this cross-linking further densifies the film, leading to smaller intermolecular distances and improved charge transport.

[0020] It is also possible to co-polymerise azulenes of the present invention with other mesogenic or liquid crystal monomers that are known from prior art, or with other reactive azulenes of the present invention, in order to induce or enhance liquid crystal phase behaviour.

[0021] Thus, another object of the invention is a polymerisable liquid crystal mixture comprising one or more reactive azulenes of the present invention, and optionally comprising one or more further reactive compounds, wherein at least one of the reactive azulenes and the further reactive compounds is mesogenic or liquid crystalline.

[0022] Particularly preferred are reactive liquid crystal azulenes of the present invention, or liquid crystal mixtures comprising one or more reactive azulenes of the present invention, that exhibit a nematic and/or smectic liquid crystal phase.

[0023] Another object of the present invention is an anisotropic polymer film with charge transport properties obtainable from a polymerisable liquid crystal mixture as defined above that is aligned in its liquid crystal phase into macroscopically ordered orientation and polymerised or cross-linked to fix the oriented state.

[0024] Another object of the invention is a liquid crystal side chain polymer (SCLCP) obtained from a polymerisable liquid crystal material as defined above by polymerisation or polymeranalogous reaction. Particularly preferred are SCLCPs obtained from one or more reactive azulenes or from a polymerisable mixture comprising one or more azulenes as described above.

[0025] Another object of the invention is an SCLCP obtained from one or more reactive azulenes or from a polymerisable liquid crystal mixture as defined above, by copolymerisation or polymeranalogous reaction together with one or more additional mesogenic or non-mesogenic comonomers.

[0026] Side chain liquid crystal polymers or copolymers (SCLCPs), in which the semiconducting component is located as a pendant group, separated from a flexible backbone by an aliphatic spacer group, offer the possibility to obtain a highly ordered lamellar like morphology. This structure consists of closely packed conjugated aromatic mesogens, in which very close (typically $< 4 \text{ \AA}$) pi-pi stacking can occur. This stacking allows intermolecular charge transport to occur more easily, leading to high charge carrier mobilities. SCLCPs are advantageous for specific applications as they can be readily synthesized before processing and then e.g. be processed from solution in an organic solvent. If SCLCPs are used in solutions, they can orient spontaneously when coated onto an appropriate surface and when at their mesophase temperature, which can result in large area, highly ordered domains.

[0027] Another object of the invention is the use of reactive mesogenic azulenes of the present invention, or liquid crystal mixtures or polymer films obtained thereof, as light-modulating component in liquid crystal displays, which may for example be switchable between two different states by an electric field, for components of liquid crystal displays, in particular optical retardation or compensation films, alignment layers or polarisers, or in other optical or electrooptical devices.

[0028] Another object of the invention is a liquid crystal display, component of a liquid crystal display, in particular an optical retardation or compensation films, alignment layer or polariser, or an other optical or electrooptical device comprising reactive azulenes according to the present invention, or liquid crystal mixtures or polymer films obtained thereof.

[0029] The azulene groups in the inventive compounds are preferably linked to their neighbouring groups at the 2- and 6-position.

[0030] Especially preferred are compounds selected of formula I



wherein

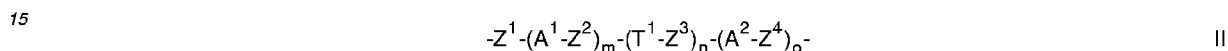
P is a polymerisable or reactive group,

Sp is a spacer group or a single bond,

R¹ is H, halogen, CN, NO₂, an aliphatic, alicyclic or aromatic group with up to 40 C atoms that optionally comprise one or more hetero atoms and one or more fused rings, or P-Sp-, and

T is a mesogenic group comprising one or more azulene groups that are optionally substituted and optionally comprise fused azulene groups, with the proviso that azulene groups linked to their neighbored groups at the 1- and 3-position are excluded.

- 5 **[0031]** R¹ in formula I is preferably H, F, Cl or straight chain, branched or cyclic alkyl with 1 to 20 C-atoms, which is unsubstituted, mono- or poly-substituted by F, Cl, Br, I or CN, wherein one or more non-adjacent CH₂ groups are optionally replaced, in each case independently from one another, by -O-, -S-, -NH-, -NR⁰-, -SiR⁰R⁰⁰-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -CH=CH- or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, or an aromatic or heteroaromatic group.
- 10 **[0032]** Particularly preferably R¹ is optionally fluorinated alkyl or alkoxy with 1 to 15 C atoms.
[0033] Further preferred are compounds of formula I wherein R¹ is P-Sp.
[0034] T in formula I preferably comprises 1 or 2 azulene groups.
[0035] Particularly preferably T is selected of formula II



wherein

- 20 A¹ and A² are independently of each other an aromatic, heteroaromatic, group with up to 18 C atoms which is unsubstituted, mono- or polysubstituted with R¹, and A¹ may also denote T¹,
- Z¹ to Z⁴ are independently of each other -O-, -S-, -CO-, -COO-, -OCO-, -O-COO-, -CO-NR⁰-, -NR⁰-CO-, -OCH₂-, -CH₂O-, -SCH₂-, -CH₂S-, -CF₂O-, -OCF₂-, -CF₂S-, -SCF₂-, -CH₂CH₂-, -CF₂CH₂-, -CH₂CF₂-, -CF₂CF₂-,
 25 -CH=N-, -N=CH-, -N=N-, -CH=CR⁰-, -CX¹=CX²-, -C≡C-, -CH=CH-COO-, -OCO-CH=CH- or a single bond,
- X¹ and X² are independently of each other H, F, Cl or CN,
- 30 T¹ is a group consisting of 1, 2, 3, or 4 azulene units which are optionally substituted by R²,
- R² is H, halogen, CN, NO₂, straight chain, branched or cyclic alkyl with 1 to 20 C-atoms, which is unsubstituted, mono- or poly-substituted by F, Cl, Br, I or CN, wherein one or more non-adjacent CH₂ groups are optionally replaced, in each case independently from one another, by -O-, -S-, -NH-, -NR⁰-,
 35 -SiR⁰R⁰⁰-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -CH=CH- or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, or denotes an aromatic or heteroaromatic group or P-Sp,
- R⁰ and R⁰⁰ are independently of each other H or alkyl with 1 to 12 C-atoms,
- 40 m and o are independently of each other 0, 1, 2 or 3, and
- n is 1, 2 or 3

- 45 **[0036]** Particularly preferred groups T are those wherein Z¹, A¹, Z², T¹, Z³, A² and Z⁴ form a conjugated system. Therein A¹ and A² are preferably arylene or heteroarylene and Z¹, Z², Z³ and Z⁴ are preferably a single bond or a conjugated link such as -CX¹=CX²- or -C≡C-.

[0037] Further preferred groups T are those wherein m and o are 0, further those wherein m and o are 1 or 2.

- [0038]** Further preferred groups T are those wherein T¹ is azulene that is optionally substituted with R² as defined in formula II, furthermore those wherein n is 1 or 2 and Z² is a single bond or a conjugated link such as -CX¹=CX²- or -C≡C-.

[0039] Particularly preferred groups T are those of the following formulae

55	-Z ¹ -T ¹ -Z ³ -	II1
	-Z ¹ -A ¹ -Z ² -T ¹ -Z ³ -	II2
	-Z ¹ -Z ¹ -Z ³ -T ¹ -Z ³ -	II3
	-Z ¹ -A ¹ -Z ² -T ¹ -Z ³ -A ² -Z ⁴ -	II4

(continued)

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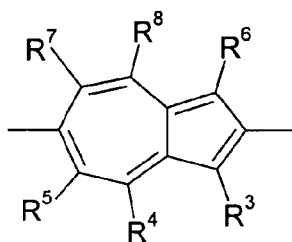
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-Z ¹ -A ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ³ -	II5
-Z ¹ -A ¹ -Z ² -T ¹ -Z ³ -T ¹ -Z ³ -	II6
-Z ¹ -T ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ³ -	II7
-Z ¹ -A ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ³ -A ² -Z ⁴ -	II8
-Z ¹ -A ¹ -Z ² -A ¹ -Z ² -A ¹ -Z ² -T ² -Z ³ -	II9
-Z ¹ -A ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ³ -T ² -Z ³ -	II10
-Z ¹ -A ¹ -Z ² -T ¹ -Z ² -A ¹ -Z ² -T ² -Z ³ -	II11
-Z ¹ -A ¹ -Z ² -T ¹ -Z ³ -T ¹ -Z ³ -A ² -Z ⁴ -	II12
-Z ¹ -T ¹ -Z ² -A ¹ -Z ² -A ¹ -Z ² -T ² -Z ³ -	II13
-Z ¹ -A ¹ -Z ² -T ¹ -Z ³ -T ¹ -Z ³ -T ¹ -Z ³ -	II14
-Z ¹ -T ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ³ -T ¹ -Z ³ -	II15
-Z ¹ -A ¹ -Z ² -A ¹ -Z ² -A ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ³ -	II16
-Z ¹ -A ¹ -Z ² -A ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ³ -A ¹ -Z ⁴ -	II17
-Z ¹ -A ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ³ -A ² -Z ⁴ -A ² -Z ⁴ -	II18
-Z ¹ -A ¹ -Z ² -A ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ³ -T ¹ -Z ³ -	II19
-Z ¹ -A ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ³ -	II20
-Z ¹ -A ¹ -Z ² -T ¹ -Z ² -A ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ³ -	II21
-Z ¹ -A ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ³ -T ¹ -Z ³ -A ² -Z ⁴ -	II22
-Z ¹ -A ¹ -Z ² -T ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ³ -A ² -Z ⁴ -	II23
-Z ¹ -T ¹ -Z ² -A ¹ -Z ² -A ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ³ -	II24
-Z ¹ -A ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ³ -T ¹ -Z ³ -T ¹ -Z ³ -	II25
-Z ¹ -A ¹ -Z ² -T ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ³ -T ¹ -Z ³ -	II26
-Z ¹ -A ¹ -Z ² -T ¹ -Z ² -T ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ³ -	II27
-Z ¹ -A ¹ -Z ² -T ¹ -Z ³ -T ¹ -Z ³ -T ¹ -Z ³ -A ² -Z ⁴ -	II28
-Z ¹ -T ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ³ -	II29
-Z ¹ -T ¹ -Z ² -A ¹ -Z ² -A ¹ -Z ² -T ¹ -Z ³ -T ¹ -Z ³ -	II30

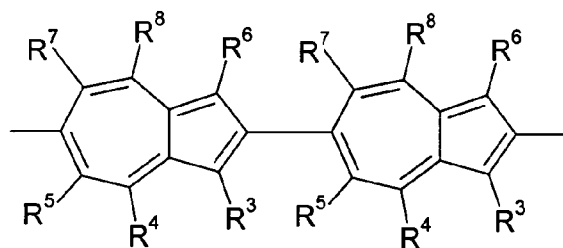
wherein Z¹, Z², Z³, Z⁴, A¹, A² and T¹ have in each case independently one of the meanings of formula II.

[0040] T¹ is preferably 2,6-azulene, furthermore [2,6']-bisazulene-6,2'-diyl, [2,2']-bisazulene-6,6'-diyl or [6,6']-bisazulene-2,2'-diyl, all of which are optionally mono- or polysubstituted by R² as defined in formula II.

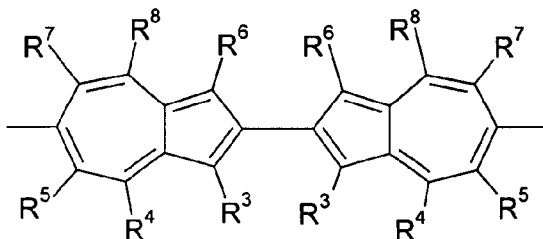
[0041] T¹ is preferably selected from the following subformulae



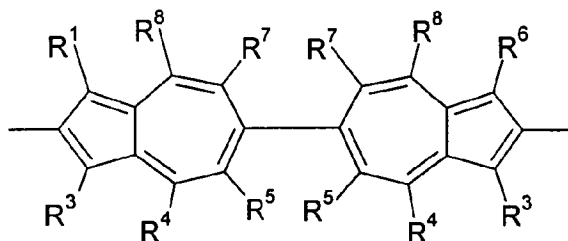
IIIa



IIIb



IIIc



IIId

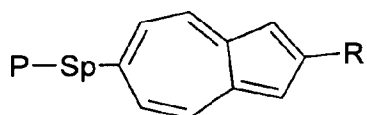
wherein R^3 to R^8 have independently of each other one of the meanings of R^1 in formula II, and are preferably halogen, methyl, ethyl, propyl, CO_2Me , CO_2Et , CN, COCH_3 or CHO.

[0042] A^1 and A^2 are preferably selected from 1,4-phenylene, 1,4-cyclohexa-1,3-diene, 1,4-cyclohexenylylene in which, in addition, one or more CH groups are optionally replaced by N and one or two non-adjacent CH_2 groups are optionally replaced by O and/or S, thiophene-2,5-diyl, thienothiophene-2,5-diyl, dithienothiophene-2,6-diyl, 1,4-bicyclo-(2,2,2)-octylene, naphthalene-2,6-diyl, furan 2,5 diyl, and indane-2,5-diyl, wherein these groups are unsubstituted, mono- or polysubstituted by L, with L being halogen, CN, SCN, NO_2 , SF_5 or an alkyl, alkoxy, alkylcarbonyl or alkoxy-carbonyl group with 1 to 4 C atoms, wherein one or more H atoms are optionally substituted with F or Cl.

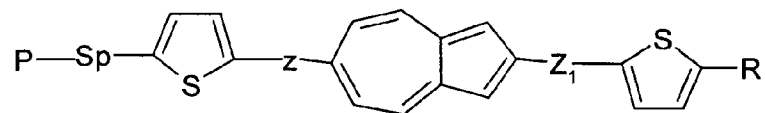
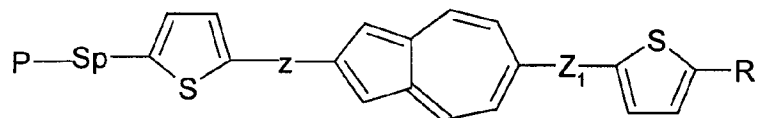
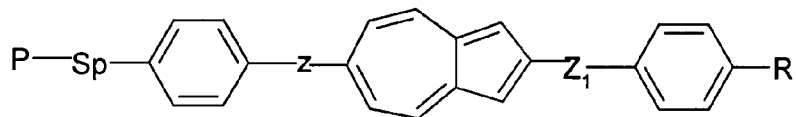
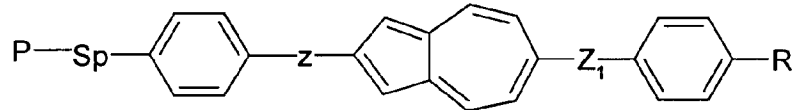
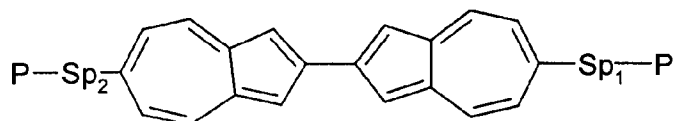
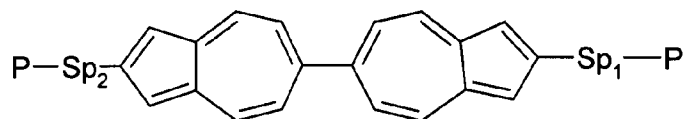
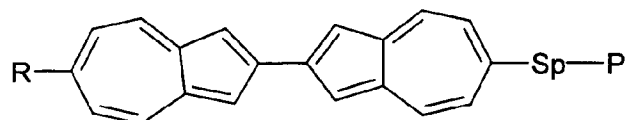
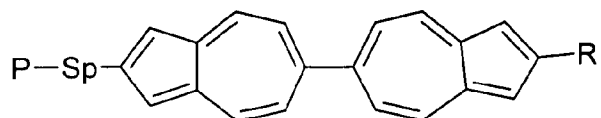
[0043] A^1 and A^2 are particularly preferably 1,4-phenylene that is substituted with 1, 2 or 3 groups L as defined above, or thiophene-2,5-diyl, all of which are optionally substituted with one or more groups L as defined above.

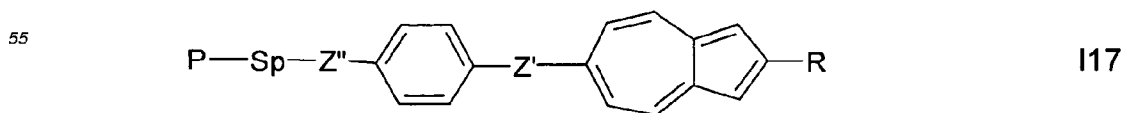
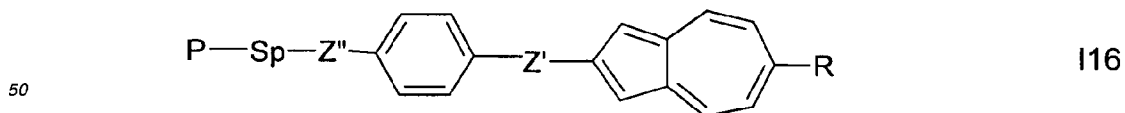
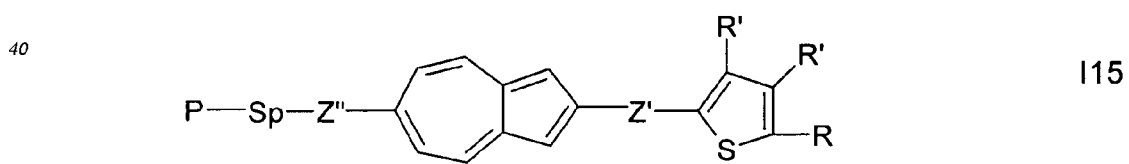
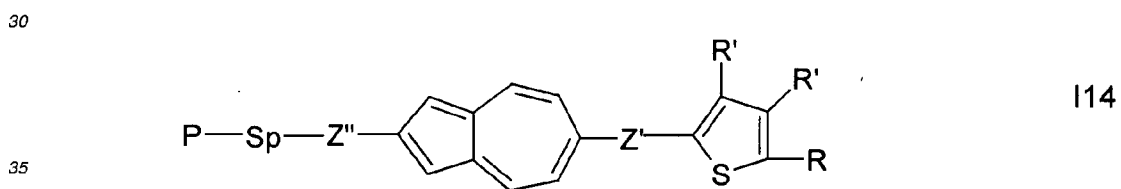
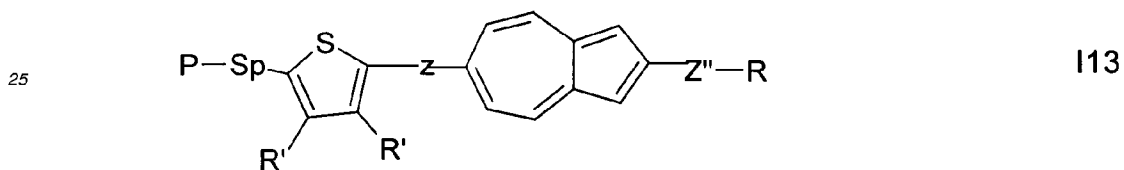
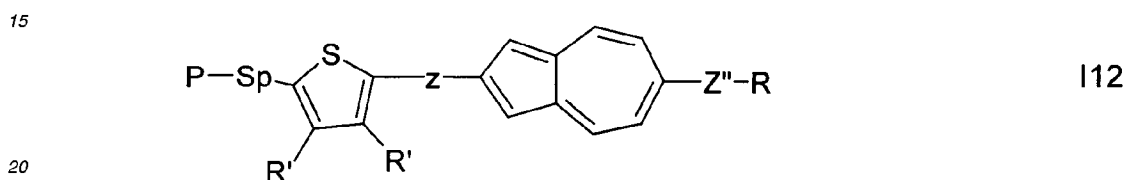
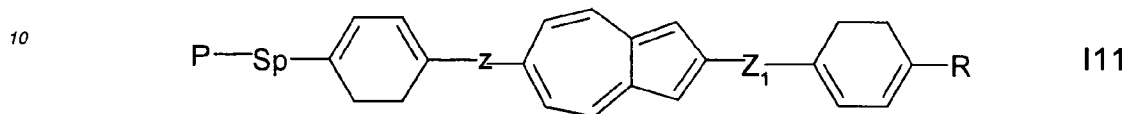
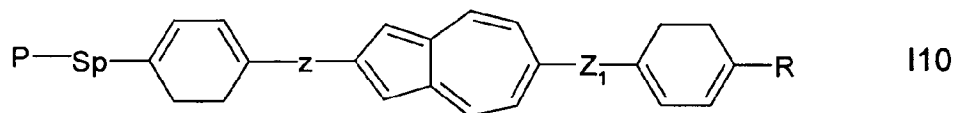
[0044] Z^{1-4} are preferably selected from $-\text{O}-$, $-\text{S}-$, $-\text{OCH}_2-$, $-\text{CH}_2\text{O}-$, $-\text{SCH}_2-$, $-\text{CH}_2\text{S}-$, $-\text{CF}_2\text{O}-$, $-\text{OCF}_2-$, $-\text{CF}_2\text{S}-$, $-\text{SCF}_2-$, $-\text{CH}_2\text{CH}_2-$, $-\text{CF}_2\text{CH}_2-$, $-\text{CH}_2\text{CF}_2-$, $-\text{CF}_2\text{CF}_2-$, $-\text{CH}=\text{N}-$, $-\text{N}=\text{CH}-$, $-\text{N}=\text{N}-$, $-\text{CH}=\text{CR}^0-$, $-\text{CX}^1=\text{CX}^2-$, $-\text{C}\equiv\text{C}-$ and a single bond, in particular from $-\text{CH}=\text{N}-$, $-\text{N}=\text{CH}-$, $-\text{N}=\text{N}-$, $-\text{CH}=\text{CR}^0-$, $-\text{CX}^1=\text{CX}^2-$, $-\text{C}\equiv\text{C}-$ and a single bond.

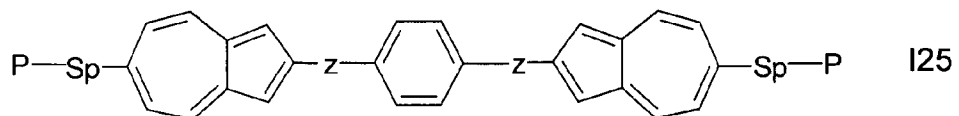
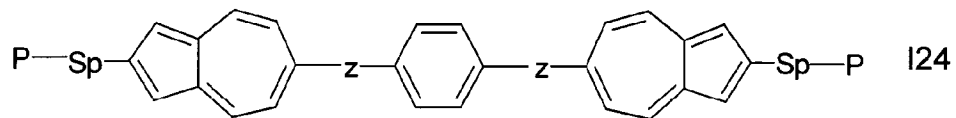
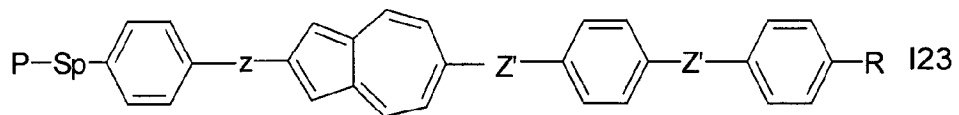
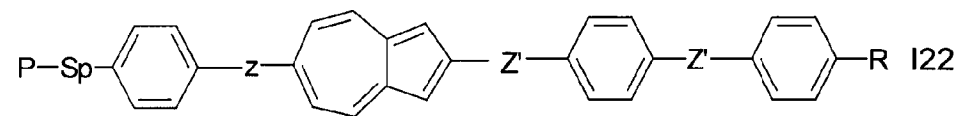
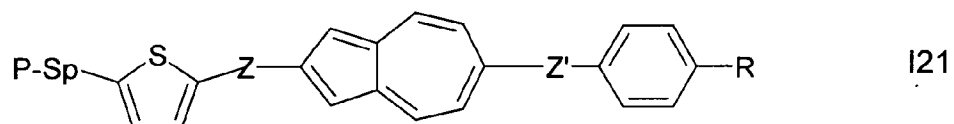
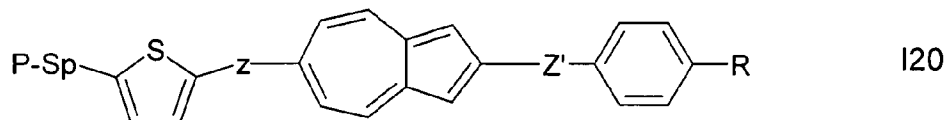
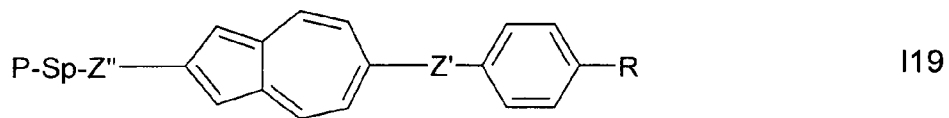
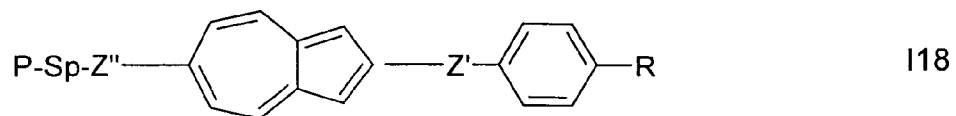
[0045] Particularly preferred are the following compounds

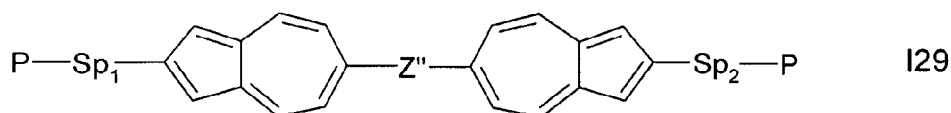
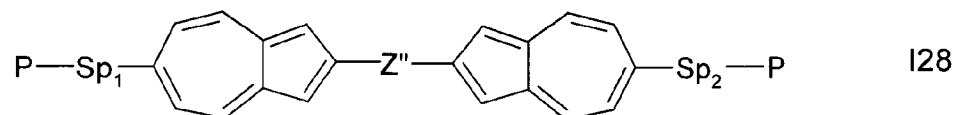
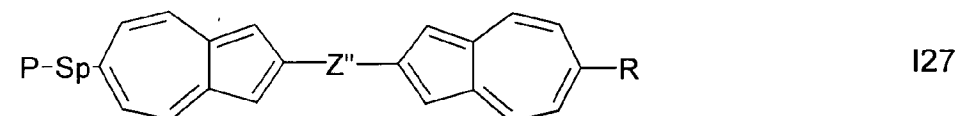
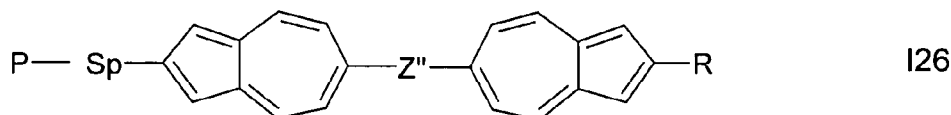


I1









wherein P, Sp and n have the meanings of formula I,

[0046] Sp¹ and Sp² are different groups Sp as defined in formula I,

Z and Z' have independently of each other one of the meanings of Z¹ in formula II, and are preferably -CH=CH-, -CH=CF-, -CF=CH-, CH=CCl-, -CCl=CH-, -CF=CF-, -CCl=CCl-, -C≡C- or a single bond,

Z'' has one of the meanings of Z¹ in formula II, and is preferably -CH=CH-, -CH=CF-, -CF=CH-, CH=CCl-, -CCl=CH-, -CF=CF-, -CCl=CCl- or -C≡C-,

R has in each case independently one of the meanings of R¹ of formula I, and is preferably halogen, an optionally fluorinated alkyl groups with 1 to 15 C atoms or P-Sp-,

R' has in each case independently one of the meanings of R² in formula II, and is preferably halogen, an optionally fluorinated alkyl group with 1 to 15 C atoms or P-Sp-,

and wherein the azulene group is optionally mono- or polysubstituted by R² as defined in formula II.

[0047] Further preferred are compounds of the preferred formulae 16 to 129, wherein the azulene-2,6-diyl groups are replaced by [2,6']-bisazulene-6,2'-diyl, [2,2']-bisazulene-6,6'-diyl or [6,6']-bisazulene-2,2'-diyl, all of which are optionally mono- or polysubstituted by R² as defined in formula II.

[0048] In the foregoing and the following, arylene and heteroarylene preferably denote a bivalent mono-, bi- or tricyclic aromatic or heteroaromatic group with up to 15 C atoms that may also comprise fused rings and is optionally substituted with one or more groups selected from H, halogen, CN, NO₂, straight chain, branched or cyclic alkyl with 1 to 20 C-atoms, which is unsubstituted, mono- or poly-substituted by F, Cl, Br, I or CN, wherein one or more non-adjacent CH₂ groups are optionally replaced, in each case independently from one another, by -O-, -S-, -NH-, -NR⁰-, -SiR⁰R⁰⁰-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -CH=CH- or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, and P-Sp as defined in formula I. Very preferred arylene and heteroarylene groups are those having one of the preferred meanings of A¹ as given above and below.

[0049] Aryl and heteroaryl preferably denote a mono-, bi- or tricyclic aromatic or heteroaromatic group with up to 25 C atoms that may also comprise fused rings and is optionally substituted with one or more groups selected from H, halogen, CN, NO₂, straight chain, branched or cyclic alkyl with 1 to 20 C-atoms, which is unsubstituted, mono- or poly-substituted by F, Cl, Br, I or CN, wherein one or more non-adjacent CH₂ groups are optionally replaced, in each case

independently from one another, by -O-, -S-, -NH-, -NR⁰-, -SiR⁰R⁰⁰-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -CH=CH- or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, and P-Sp as defined in formula I.

[0050] Especially preferred aryl and heteroaryl groups are phenyl in which, in addition, one or more CH groups are optionally replaced by N, naphthalene, thiophene, thienothiophene, dithienothiophene, alkyl fluorene and oxazole, all of which can be unsubstituted, mono- or polysubstituted with L, wherein L is halogen or an alkyl, alkoxy, alkylcarbonyl or alkoxycarbonyl group with 1 to 12 C atoms, wherein one or more H atoms are optionally replaced by F or Cl.

[0051] Further preferred aryl and heteroaryl groups include five-membered heterocyclics like oxazole or isoxazole, N-substituted imidazole or pyrazole, thiazole or isothiazole, oxadiazole, N-substituted triazole, six-membered heterocyclics like pyridine, pyridazine, pyrimidine, pyrazine, triazine and tetrazine, heterocyclics with fused rings like benzoxazole, benzothiazole, benzimidazole, quinoline, isoquinoline, cinnoline, quinazoline, quinoxaline, phthalazine, benzothiadiazole, benzotriazole, benzotriazine, phenazine, phenanthridine, acridine, or condensed polycyclics like acenaphthene, phenanthrene, anthracene, fluoranthene, pyrene, perylene, rubrene, chrysene, naphthacene, coronene or triphenylene, all of which can be unsubstituted, mono- or polysubstituted with L as defined above.

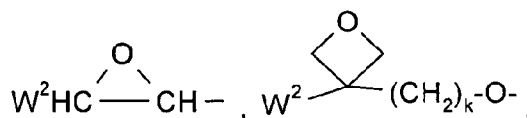
[0052] -CX¹=CX²- is preferably -CH=CH-, -CH=CF-, -CF=CH-, -CF=CF-, -CH=C(CN)- or -C(CN)=CH-.

[0053] If one of R¹ to R⁸ is an alkyl or alkoxy radical, i.e. where the terminal CH₂ group is replaced by -O-, this may be straight-chain or branched. It is preferably straight-chain, has 2, 3, 4, 5, 6, 7 or 8 carbon atoms and accordingly is preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, or octoxy, furthermore methyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, nonoxy, decoxy, undecoxy, do-decoxy, tridecoxy or tetradecoxy, for example.

[0054] Oxaalkyl, i.e. where one CH₂ group is replaced by -O-, is preferably straight-chain 2-oxapropyl (=methoxymethyl), 2- (=ethoxymethyl) or 3-oxabutyl (=2-methoxyethyl), 2-, 3-, or 4-oxapentyl, 2-, 3-, 4-, or 5-oxahexyl, 2-, 3-, 4-, 5-, or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl or 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl, for example.

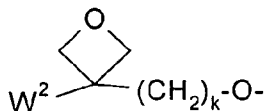
[0055] Halogen is preferably F or Cl.

[0056] The polymerisable or reactive group P is preferably selected from CH₂=CW¹-COO-,



CH₂=CW²-(O)_{k1}-, CH₃-CH=CH-O-, HO-CW²W³-, HS-CW²W³-, HW²N-, HO-CW²W³-NH-, CH₂=CW¹-CO-NH-, CH₂=CH-(COO)_{k1}-Phe-(O)_{k2}-, Phe-CH=CH-, HOOC-, OCN- and W⁴W⁵W⁶Si-, with W¹ being H, Cl, CN, phenyl or alkyl with 1 to 5 C-atoms, in particular H, Cl or CH₃, W² and W³ being independently of each other H or alkyl with 1 to 5 C-atoms, in particular methyl, ethyl or n-propyl, W⁴, W⁵ and W⁶ being independently of each other Cl, oxaalkyl or oxacarbonylalkyl with 1 to 5 C-atoms, Phe being 1,4-phenylene and k₁ and k₂ being independently of each other 0 or 1.

[0057] Especially preferred groups P are CH₂=CH-COO-, CH₂=C(CH₃)-COO-, CH₂=CH-, CH₂=CH-O- and



[0058] Very preferred are acrylate and oxetane groups. Oxetanes produce less shrinkage upon polymerisation (cross-linking), which results in less stress development within films, leading to higher retention of ordering and fewer defects. Oxetane cross-linking also requires cationic initiator, which unlike free radical initiator is inert to oxygen.

[0059] As for the spacer group Sp all groups can be used that are known for this purpose to those skilled in the art. The spacer group Sp is preferably a linear or branched alkylene group having 1 to 20 C atoms, in particular 1 to 12 C atoms, in which, in addition, one or more non-adjacent CH₂ groups are optionally replaced by -O-, -S-, -NH-, -N(CH₃)-, -CO-, -O-CO-, -S-CO-, -O-COO-, -CO-S-, -CO-O-, -CH(halogen)-, -C(halogen)₂-, -CH(CN)-, -CH=CH- or -C≡C-, or a siloxane group.

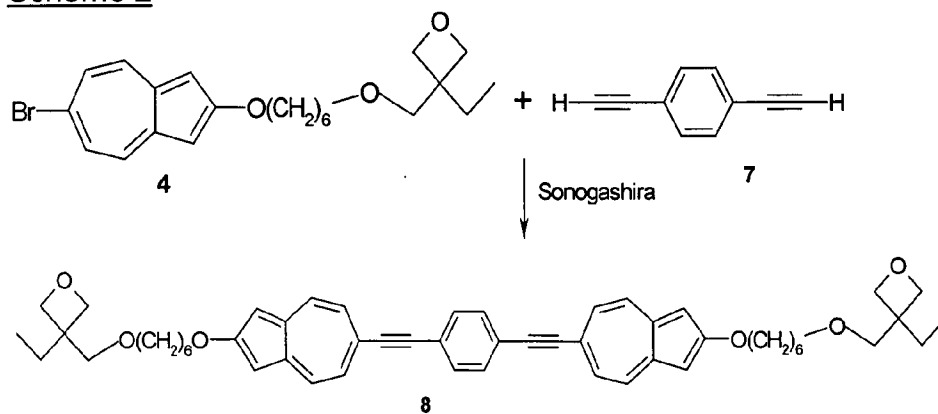
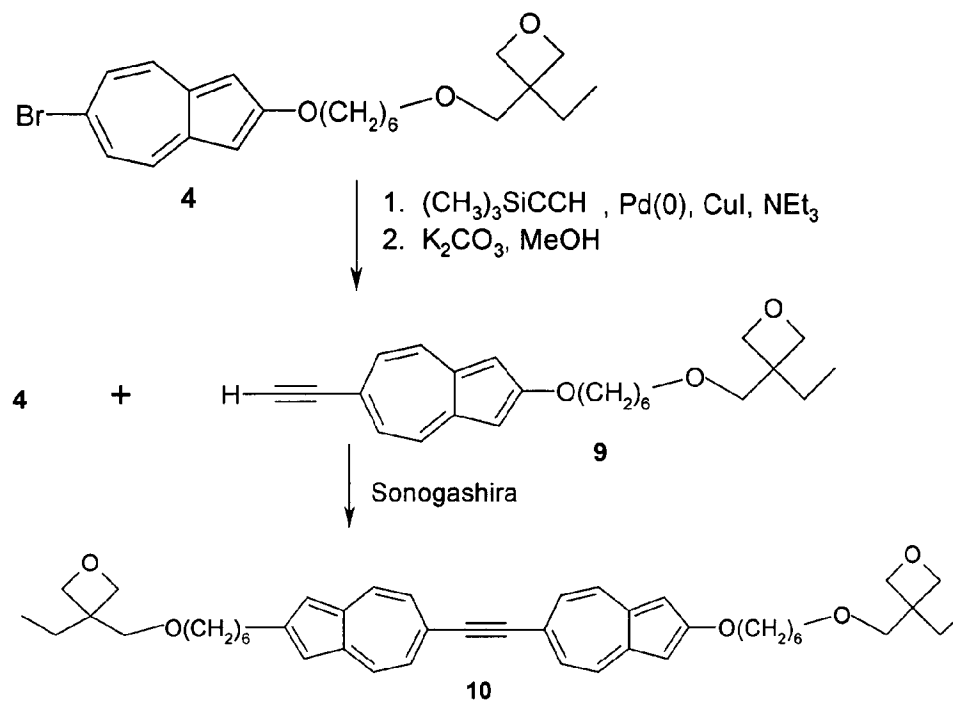
[0060] Typical spacer groups are for example -(CH₂)_p-, -(CH₂CH₂O)_r-CH₂CH₂-, -CH₂CH₂-S-CH₂CH₂- or -CH₂CH₂-NH-CH₂CH₂- or -(SiR⁰R⁰⁰-O)_p-, with p being an integer from 2 to 12, r being an integer from 1 to 3 and R⁰ and R⁰⁰ having the meanings given in formula I.

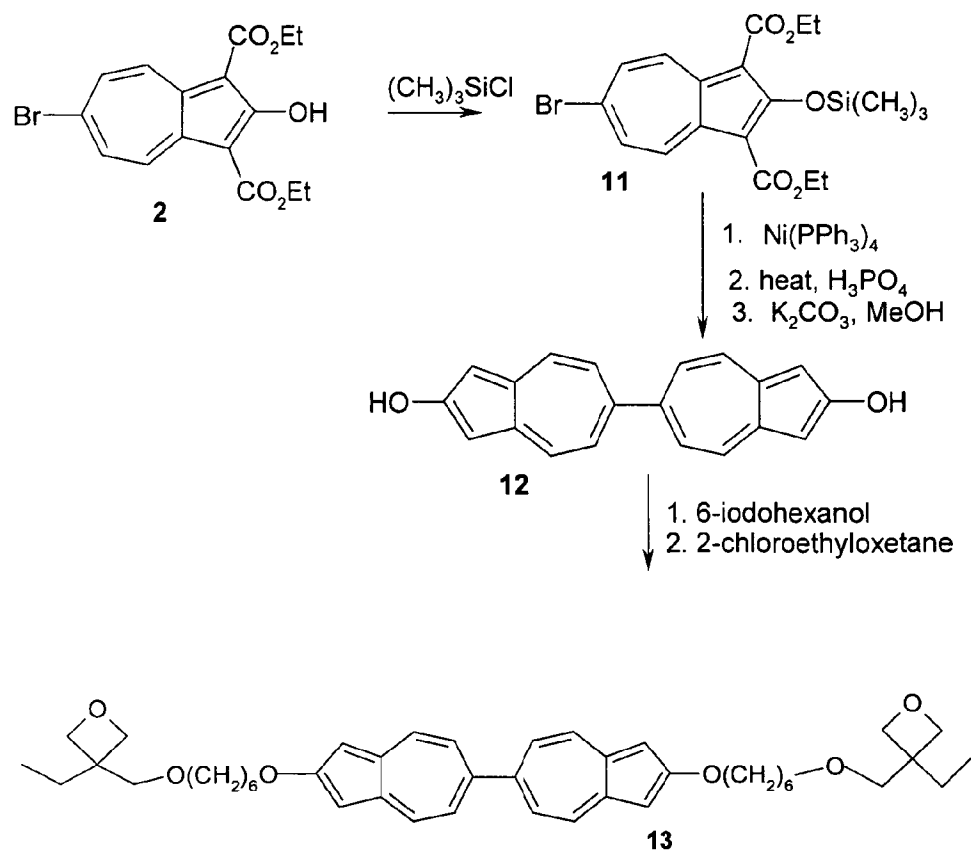
[0061] Preferred spacer groups are ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, non-

[0062] Further preferred are compounds with one or two groups P-Sp-X wherein Sp and/or X is a single bond.

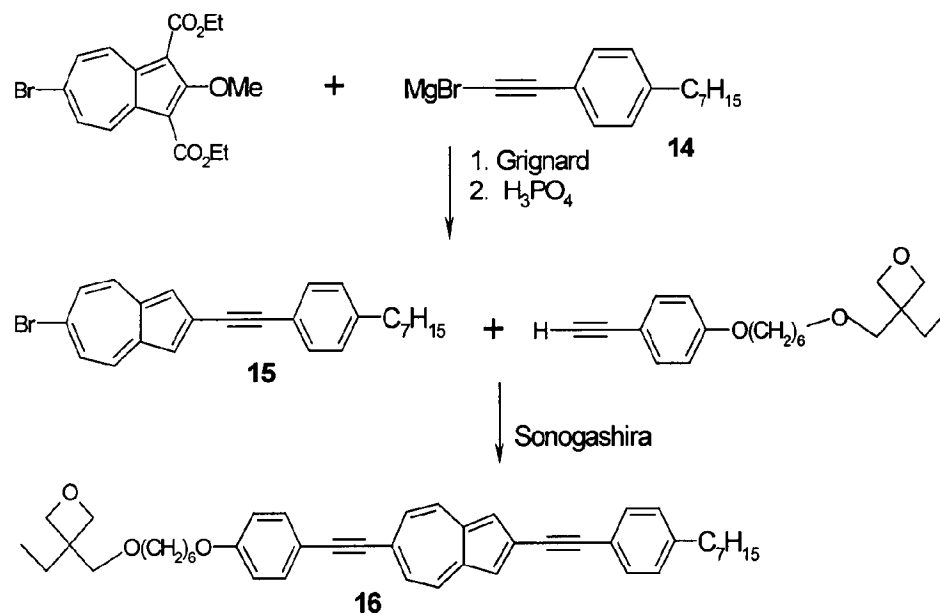
[0064] SCLCPs obtained from the inventive compounds or mixtures by polymerisation or copolymerisation have a backbone that is formed by the polymerisable group P in formula I.

[0065] The compounds of formula I can be synthesized according to or in analogy to methods that are known to the skilled in the art and are described for example in T. Nozoe, T. Asao and M. Oda, *Bull. Chem. Soc. Jpn.* 1974, 47, 681; D. Balschukat and E. V. Dehmlow, *Chem. Ber.*, 1986, 119, 2272-2288 and T. Morita and K. Takase, *Bull. Chem. Soc. Jpn.*, 1982, 55, 1144-1152 and T. Nozoe, S. Seto and S. Matsumura, *Bull. Chem. Soc. Jpn.*, 1962, 35, 1990. Furthermore, they can be prepared according to or in analogy to the following reaction schemes.

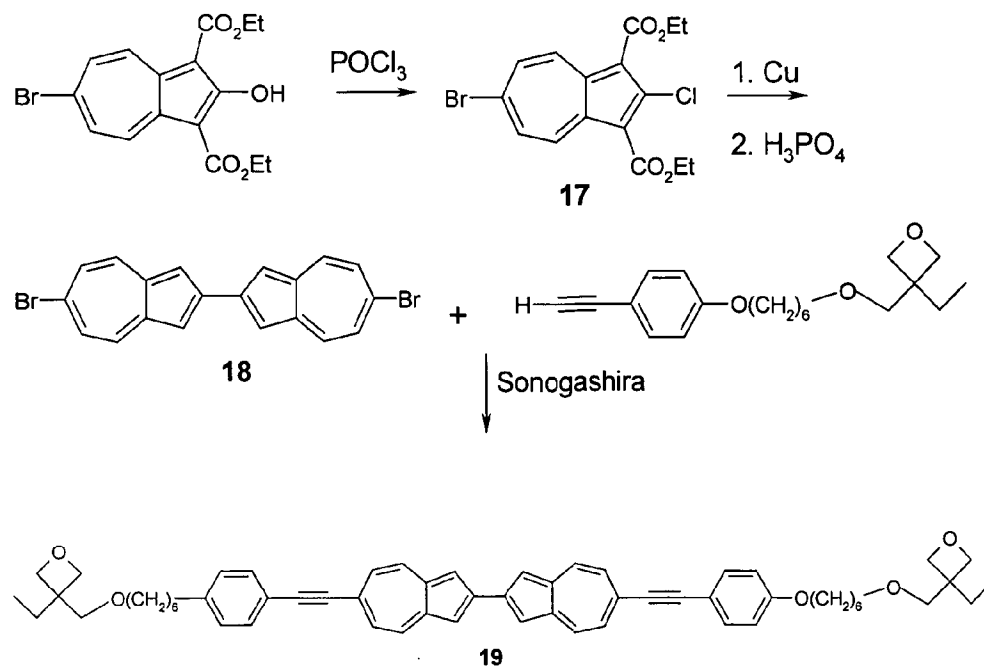
Scheme 2**Scheme 3**

Scheme 4

Scheme 5

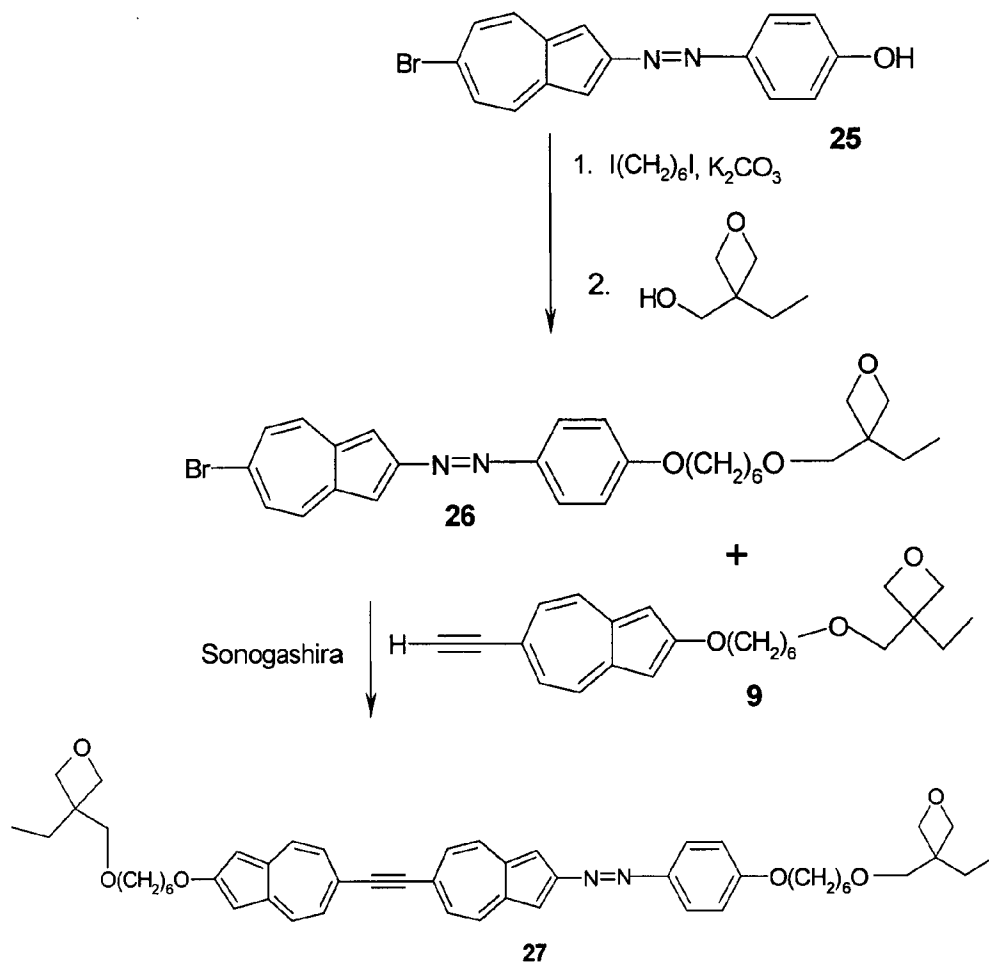


Scheme 6

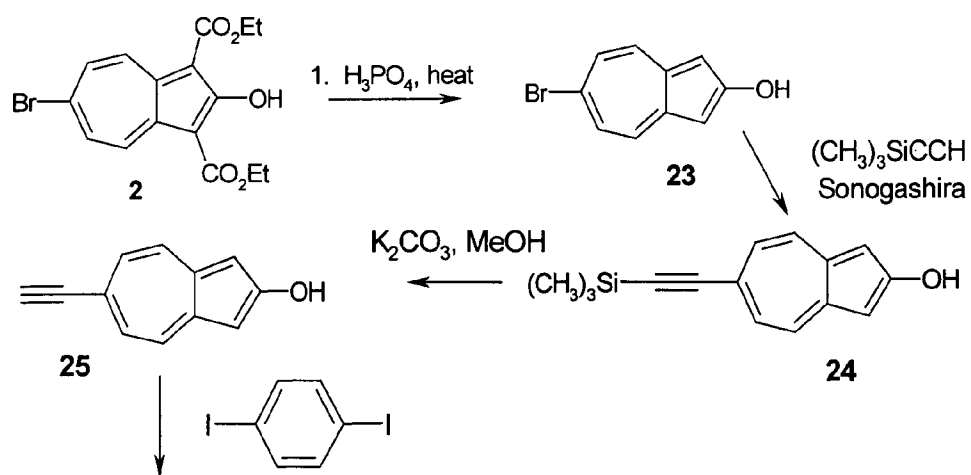


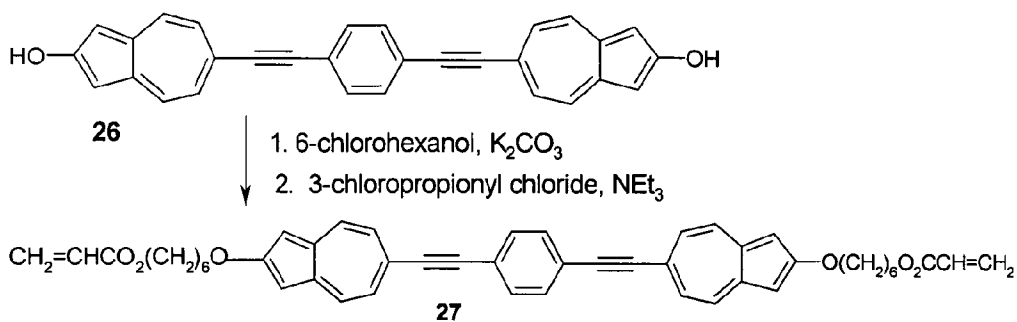
Scheme 8





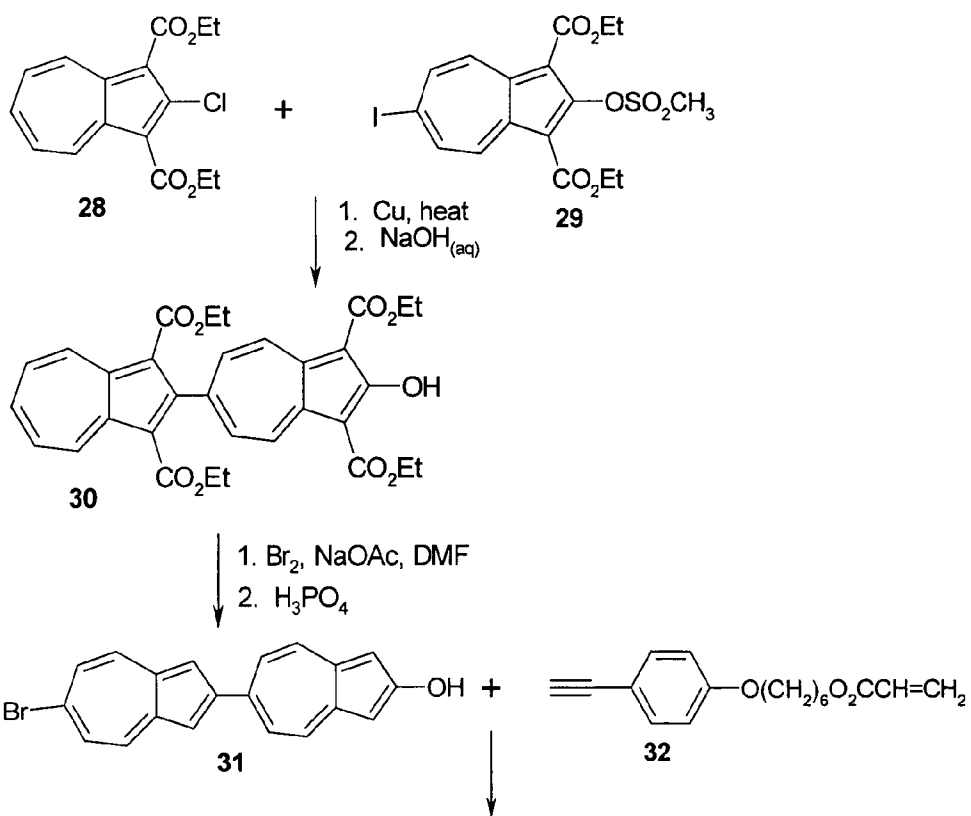
Scheme 9

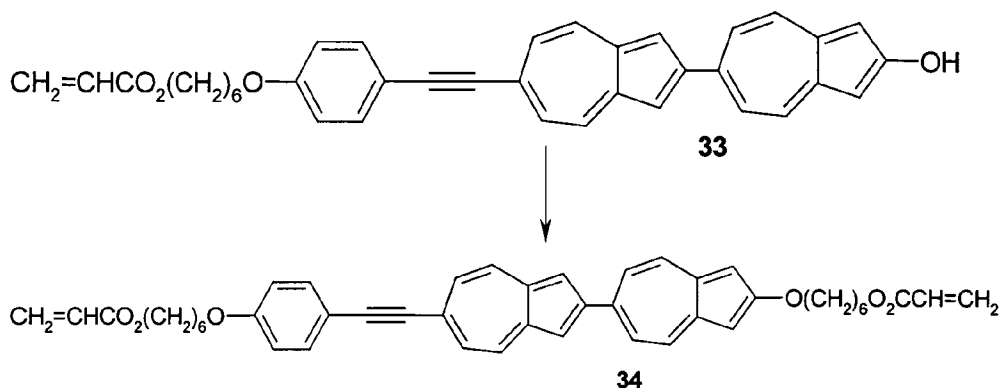




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Scheme 10





[0066] A preferred embodiment of the present invention relates to reactive azulenenes, in particular those of formula I, that are mesogenic or liquid crystalline. These materials are particularly useful as semiconductors or charge transport materials, as they can be aligned into uniform highly ordered orientation in their liquid crystal phase by known techniques, thus exhibiting a higher degree of order that leads to particularly high charge carrier mobility. The highly ordered liquid crystal state can be fixed by in situ polymerisation or crosslinking via the groups P to yield polymer films with high charge carrier mobility and high thermal, mechanical and chemical stability.

[0067] It is also possible to copolymerise the azulenenes according to the present invention with other polymerisable mesogenic or liquid crystal monomers that are known from prior art, in order to induce or enhance liquid crystal phase behaviour.

[0068] Thus, another object of the invention is a polymerisable liquid crystal material comprising one or more reactive azulenenes of the present invention as described above and below comprising at least one reactive group, and optionally comprising one or more further reactive compounds, wherein at least one of the reactive azulenenes of the present invention and/or the further reactive compounds is mesogenic or liquid crystalline.

[0069] Particularly preferred are liquid crystal materials having a nematic and/or smectic phase. For FET applications smectic materials are especially preferred. For OLED applications nematic or smectic materials are especially preferred.

[0070] Another object of the present invention is an anisotropic polymer film with charge transport properties obtainable from a polymerisable liquid crystal material as defined above that is aligned in its liquid crystal phase into macroscopically uniform orientation and polymerised or crosslinked to fix the oriented state.

[0071] Polymerisation is preferably carried out by in-situ polymerisation of a coated layer of the material, preferably during fabrication of the electronic or optical device comprising the inventive semiconductor material. In case of liquid crystal materials, these are preferably aligned in their liquid crystal state into homeotropic orientation prior to polymerisation, where the conjugated pi-electron systems are orthogonal to the direction of charge transport. This ensures that the intermolecular distances are minimised and hence then energy required to transport charge between molecules is minimised. The molecules are then polymerised or crosslinked to fix the uniform orientation of the liquid crystal state. Alignment and curing are carried out in the liquid crystal phase or mesophase of the material. This technique is known in the art and is generally described for example in D.J. Broer, et al., Angew. Makromol. Chem. 183, (1990), 45-66

[0072] Alignment of the liquid crystal material can be achieved for example by treatment of the substrate onto which the material is coated, by shearing the material during or after coating, by application of a magnetic or electric field to the coated material, or by the addition of surface-active compounds to the liquid crystal material. Reviews of alignment techniques are given for example by I. Sage in "Thermotropic Liquid Crystals", edited by G. W. Gray, John Wiley & Sons, 1987, pages 75-77, and by T. Uchida and H. Seki in "Liquid Crystals - Applications and Uses Vol. 3", edited by B. Bahadur, World Scientific Publishing, Singapore 1992, pages 1-63. A review of alignment materials and techniques is given by J. Cognard, Mol. Cryst. Liq. Cryst. 78, Supplement 1 (1981), pages 1-77.

[0073] Polymerisation takes place by exposure to heat or actinic radiation. Actinic radiation means irradiation with light, like UV light, IR light or visible light, irradiation with X-rays or gamma rays or irradiation with high energy particles, such as ions or electrons. Preferably polymerisation is carried out by UV irradiation at a non-absorbing wavelength. As a source for actinic radiation for example a single UV lamp or a set of UV lamps can be used. When using a high lamp power the curing time can be reduced. Another possible source for actinic radiation is a laser, like e.g. a UV laser, an IR laser or a visible laser.

[0074] Polymerisation is preferably carried out in the presence of an initiator absorbing at the wavelength of the actinic radiation. For example, when polymerising by means of UV light, a photoinitiator can be used that decomposes

under UV irradiation to produce free radicals or ions that start the polymerisation reaction. When curing polymerisable materials with acrylate or methacrylate groups, preferably a radical photoinitiator is used, when curing polymerisable materials with vinyl, epoxide and oxetane groups, preferably a cationic photoinitiator is used. It is also possible to use a polymerisation initiator that decomposes when heated to produce free radicals or ions that start the polymerisation.

5 As a photoinitiator for radical polymerisation for example the commercially available Irgacure 651, Irgacure 184, Darocure 1173 or Darocure 4205 (all from Ciba Geigy AG) can be used, whereas in case of cationic photopolymerisation the commercially available UVI 6974 (Union Carbide) can be used.

[0075] The polymerisable material can additionally comprise one or more other suitable components such as, for example, catalysts, sensitizers, stabilizers, inhibitors, chain-transfer agents, co-reacting monomers, surface-active compounds, lubricating agents, wetting agents, dispersing agents, hydrophobing agents, adhesive agents, flow improvers, defoaming agents, deaerators, diluents, reactive diluents, auxiliaries, colourants, dyes or pigments.

[0076] Reactive azulenes comprising one or more groups P-Sp-X can also be copolymerised with polymerisable mesogenic compounds to induce, or, in case of mesogenic materials of formula I, enhance liquid crystal phase behaviour. Polymerisable mesogenic compounds that are suitable as comonomers are known in prior art and disclosed for example in WO 93/22397; EP 0,261,712; DE 195,04,224; WO 95/22586 and WO 97/00600.

[0077] SCLCPs can be prepared from the polymerisable compounds or mixtures according to the invention by the methods described above, or by conventional polymerisation techniques which are known to those skilled in the art, including for example radicalic, anionic or cationic chain polymerisation, polyaddition or polycondensation. Polymerisation can be carried out for example as polymerisation in solution, without the need of coating and prior alignment, or polymerisation in situ. It is also possible to form SCLCPs by grafting compounds according to the invention with a suitable reactive group, or mixtures thereof, to presynthesized isotropic or anisotropic polymer backbones in a polymeranalogous reaction. For example, compounds with a terminal hydroxy group can be attached to polymer backbones with lateral carboxylic acid or ester groups, compounds with terminal isocyanate groups can be added to backbones with free hydroxy groups, compounds with terminal vinyl or vinyloxy groups can be added e.g. to polysiloxane backbones with Si-H groups. It is also possible to form SCLCPs by copolymerisation or polymeranalogous reaction from the inventive compounds together with conventional mesogenic or non mesogenic comonomers. Suitable comonomers are known to those skilled in the art. In principle it is possible to use all conventional comonomers known in the art that carry a reactive or polymerisable group capable of undergoing the desired polymer-forming reaction, like for example a polymerisable or reactive group P as defined above. Typical mesogenic comonomers are for example those mentioned in WO 93/22397; EP 0,261,712; DE 195,04,224; WO 95/22586 and WO 97/00600. Typical non mesogenic comonomers are for example alkyl mono- or diacrylates or alkyl mono- or dimethacrylates with alkyl groups of 1 to 20 C atoms, like methyl acrylate or methyl methacrylate, trimethylpropane trimethacrylate or pentaerythritol tetraacrylate.

[0078] The materials of the present invention are useful as optical, electronic and semiconductor materials, in particular as charge transport materials in field effect transistors (FETs) e.g. as components of integrated circuitry, ID tags or TFT applications. Alternatively, they may be used in organic light emitting diodes (OLEDs) in electroluminescent display applications or as backlight of e.g. liquid crystal displays, as photovoltaics or sensor materials, for electrophotographic recording, and for other semiconductor applications.

[0079] Especially the oligomers and polymers according to the invention show advantageous solubility properties which allow production processes using solutions of these compounds. Thus films, including layers and coatings, may be generated by low cost production techniques e.g. spin coating. Suitable solvents or solvent mixtures comprise alkanes and/ or aromatics, especially their fluorinated derivatives.

[0080] The materials of the present invention are useful as optical, electronic and semiconductor materials, in particular as charge transport materials in field effect transistors (FETs), as photovoltaics or sensor materials, for electrophotographic recording, and for other semiconductor applications. Such FETs, where an organic semiconductive material is arranged as a film between a gate-dielectric and a drain and a source electrode, are generally known e.g. from US 5,892,244, WO 00/79617, US 5,998,804, and from the references cited in the background and prior art chapter and listed below. Due to the advantages, like low cost production using the solubility properties of the compounds according to the invention and thus the processibility of large surfaces, preferred applications of these FETs are such as integrated circuitry, TFT-displays and security applications.

[0081] In security applications, field effect transistors and other devices with semiconductive materials, like transistors or diodes, may be used for ID tags or security markings to authenticate and prevent counterfeiting of documents of value like banknotes, credit cards or ID cards, national ID documents, licenses or any product with money value, like stamps, tickets, shares, cheques etc..

[0082] Alternatively, the materials according to the invention may be used in organic light emitting devices or diodes (OLEDs), e.g. in display applications or as backlight of e.g. liquid crystal displays. Common OLEDs are realized using multilayer structures. An emission layer is generally sandwiched between one or more electron-transport and/or hole-transport layers. By applying an electric voltage electrons and holes as charge carriers move towards the emission layer where their recombination leads to the excitation and hence luminescence of the lumophor units contained in the

emission layer. The inventive compounds, materials and films may be employed in one or more of the charge transport layers and/ or in the emission layer, corresponding to their electrical and/ or optical properties. Furthermore their use within the emission layer is especially advantageous, if the compounds, materials and films according to the invention show electroluminescent properties themselves or comprise electroluminescent groups or compounds. The selection, characterization as well as the processing of suitable monomeric, oligomeric and polymeric compounds or materials for the use in OLEDs is generally known by a person skilled in the art, see e. g. Meerholz, Synthetic Materials, 111-112, 2000, 31-34, Alcalá, J. Appl. Phys., 88, 2000, 7124-7128 and the literature cited therein.

[0083] According to another use, the inventive compounds, materials or films, especially those which show photoluminescent properties, may be employed as materials of light sources, e.g. of display devices such as described in EP 0 889 350 A1 or by C. Weder et al., Science, 279, 1998, 835-837.

[0084] A further aspect of the invention relates to both the oxidised and reduced form of the compounds and materials according to this invention. Either loss or gain of electrons results in formation of a highly delocalised ionic form, which is of high conductivity. This can occur on exposure to common dopants. Suitable dopants and methods of doping are known to those skilled in the art, e.g. from EP 0 528 662, US 5,198,153 or WO 96/21659.

[0085] The doping process typically implies treatment of the semiconductor material with an oxidating or reducing agent in a redox reaction to form delocalised ionic centres in the material, with the corresponding counterions derived from the applied dopants. Suitable doping methods comprise for example exposure to a doping vapor in the atmospheric pressure or at a reduced pressure, electrochemical doping in a solution containing a dopant, bringing a dopant into contact with the semiconductor material to be thermally diffused, and ion-implantation of the dopant into the semiconductor material.

[0086] When electrons are used as carriers, suitable dopants are for example halogens (e.g. I₂, Cl₂, Br₂, ICl, ICl₃, IBr and IF), Lewis acids (e.g. PF₅, AsF₅, SbF₅, BF₃, BCl₃, SbCl₅, BBr₃ and SO₃), protonic acids, organic acids, or amino acids (e.g. HF, HCl, HNO₃, H₂SO₄, HClO₄, FSO₃H and ClSO₃H), transition metal compounds (e.g. FeCl₃, FeOCl, Fe(ClO₄)₃, Fe(4-CH₃C₆H₄SO₃)₃, TiCl₄, ZrCl₄, HfCl₄, NbF₅, NbCl₅, TaCl₅, MoF₅, MoCl₅, WF₅, WCl₆, UF₆ and LnCl₃ (wherein Ln is a lanthanoid), anions (e.g. Cl⁻, Br⁻, I⁻, I₃⁻, HSO₄⁻, SO₄²⁻, NO₃⁻, ClO₄⁻, BF₄⁻, PF₆⁻, AsF₆⁻, SbF₆⁻, FeCl₄⁻, Fe(CN)₆³⁻, and anions of various sulfonic acids, such as aryl-SO₃⁻). When holes are used as carriers, examples of dopants are cations (e.g. H⁺, Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺), alkali metals (e.g., Li, Na, K, Rb, and Cs), alkaline-earth metals (e.g., Ca, Sr, and Ba), O₂, XeOF₄, (NO₂⁺) (SbF₆⁻), (NO₂⁺) (SbCl₆⁻), (NO₂⁺) (BF₄⁻), AgClO₄, H₂IrCl₆, La(NO₃)₃·6H₂O, FSO₂OOSO₂F, Eu, acetylcholine, R₄N⁺, (R is an alkyl group), R₄P⁺ (R is an alkyl group), R₆As⁺ (R is an alkyl group), and R₃S⁺ (R is an alkyl group).

[0087] The conducting form of the compounds and materials of the present invention can be used as an organic "metal" in applications, for example, but not limited to, charge injection layers and ITO planarising layers in organic light emitting diode applications, films for flat panel displays and touch screens, antistatic films, printed conductive substrates, patterns or tracts in electronic applications such as printed circuit boards and condensers.

Claims

1. Reactive mesogenic azulenes, consisting of a central mesogenic core comprising one or more azulene groups, and optionally comprising further unsaturated organic groups that form a conjugated system together with the azulene groups, said mesogenic core being linked, optionally via spacer groups, to one or more reactive groups.

2. Reactive mesogenic azulenes according to claim 1, **characterized in that** they are selected of formula I



I

wherein

P is a polymerisable or reactive group,

Sp is a spacer group or a single bond,

R¹ is H, halogen, CN, NO₂, an aliphatic, alicyclic or aromatic group with up to 40 C atoms that optionally comprises one or more hetero atoms and one or more fused rings, or P-Sp-, and

T is a mesogenic group comprising one or more azulene groups that are optionally substituted and optionally

comprise fused azulene groups, with the proviso that azulene groups linked to their neighboured groups at the 1-and 3-position are excluded.

3. Reactive mesogenic azulenenes according to claim 2, **characterized in that** T is selected of formula II



wherein

A¹ and A² are independently of each other an aromatic, heteroaromatic, group with up to 18 C atoms which is unsubstituted, mono- or polysubstituted with R¹, and A¹ may also denote T¹,

Z¹ to Z⁴ are independently of each other -O-, -S-, -CO-, -COO-, -OCO-, -O-COO-, -CO-NR⁰-, -NR⁰-CO-, -OCH₂-, -CH₂O-, -SCH₂-, -CH₂S-, -CF₂O-, -OCF₂-, -CF₂S-, -SCF₂-, -CH₂CH₂-, -CF₂CH₂-, -CH₂CF₂-, -CF₂CF₂-, -CH=N-, -N=CH-, -N=N-, -CH=CR⁰-, -CX¹=CX²-, -C≡C-, -CH=CH-COO-, -OCO-CH=CH- or a single bond,

X¹ and X² are independently of each other H, F, Cl or CN,

T¹ is a group consisting of 1, 2, 3, or 4 azulene groups which are optionally substituted by R²,

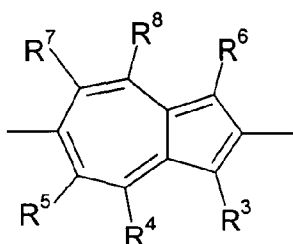
R² is H, halogen, CN, NO₂, straight chain, branched or cyclic alkyl with 1 to 20 C-atoms, which is unsubstituted, mono- or poly-substituted by F, Cl, Br, I or CN, wherein one or more non-adjacent CH₂ groups are optionally replaced, in each case independently from one another, by -O-, -S-, -NH-, -NR⁰-, -SiR⁰R⁰⁰-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -CH=CH- or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, or denotes an aromatic or heteroaromatic group or P-Sp as defined in formula I,

R⁰ and R⁰⁰ are independently of each other H or alkyl with 1 to 12 C-atoms,

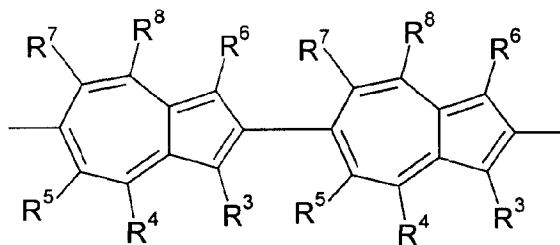
m and o are independently of each other 0, 1, 2 or 3, and

n is 1, 2 or 3.

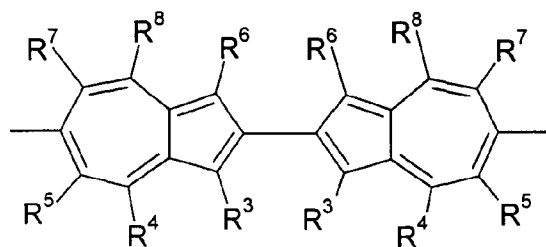
4. Reactive mesogenic azulenenes according to claim 3, **characterized in that** T¹ is selected of the following subformulae



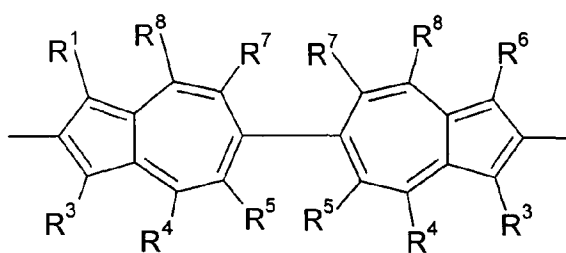
IIIa



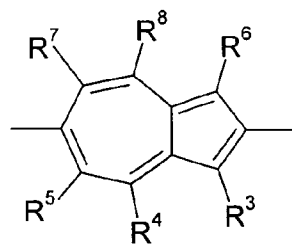
IIIb



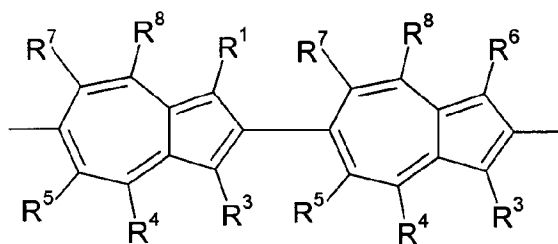
IIIc



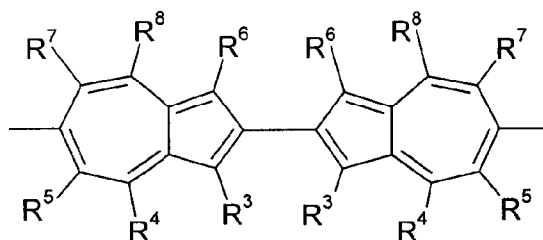
III d



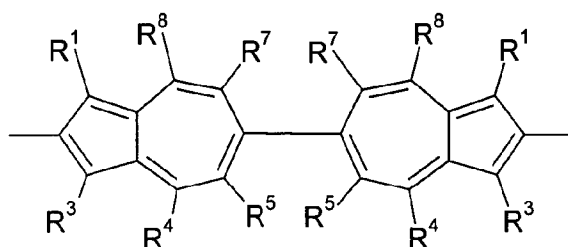
IIIa



IIIb



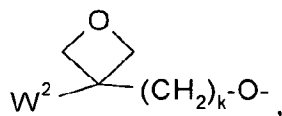
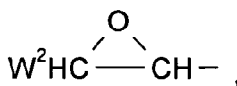
IIIc



IIIId

wherein R^3 to R^8 have independently of each other one of the meanings of R^2 in formula II.

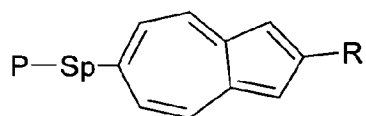
5. Reactive mesogenic azulenes according to claim 3 and/or 4, **characterized in that** A^1 and A^2 are selected from 1,4-phenylene, 1,4-cyclohexa-1,3-diene, 1,4-cyclohexenylenes in which, in addition, one or more CH groups are optionally replaced by N and one or two non-adjacent CH_2 groups are optionally replaced by O and/or S, thiophene-2,5-diyl, thienothiophene-2,5-diyl, dithienothiophene-2,6-diyl, 1,4-bicyclo-(2,2,2)-octylene, naphthalene-2,6-diyl, furan 2,5-diyl, and indane-2,5-diyl, wherein these groups are unsubstituted, mono- or polysubstituted by L, with L being halogen, CN, SCN, NO_2 , SF_5 or an alkyl, alkoxy, alkylcarbonyl or alkoxycarbonyl group with 1 to 4 C atoms, wherein one or more H atoms are optionally substituted with F or Cl.
6. Reactive mesogenic azulenes according to at least one of claims 2 to 5, **characterized in that** R is H, F, Cl or straight chain, branched or cyclic alkyl with 1 to 20 C-atoms, which is unsubstituted, mono- or poly-substituted by F, Cl, Br, I or CN, wherein one or more non-adjacent CH_2 groups are optionally replaced, in each case independently from one another, by -O-, -S-, -NH-, $-NR^{00}$ -, $-SiR^{00}R^{00}$ -, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -CH=CH- or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, or an aromatic or heteroaromatic group
7. Reactive mesogenic azulenes according to at least one of claims 1 to 6, **characterized in that** the reactive group or the group P is selected from $CH_2=CW^1-COO$ -,



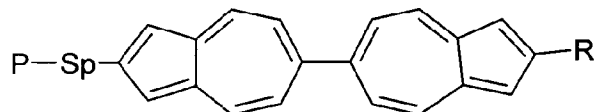
$CH_2=CW^2-(O)_{k1}$ -, $CH_3-CH=CH-O$ -, $HO-CW^2W^3$ -, $HS-CW^2W^3$ -, HW^2N -, $HO-CW^2W^3-NH$ -, $CH_2=CW^1-CO-NH$ -, $CH_2=CH-(COO)_{k1}-Phe-(O)_{k2}$ -, $Phe-CH=CH$ -, $HOOC$ -, OCN -, and $W^4W^5W^6Si$ -, with W^1 being H, Cl, CN, phenyl or alkyl with 1 to 5 C-atoms, in particular H, Cl or CH_3 , W^2 and W^3 being independently of each other H or alkyl with 1 to 5 C-atoms, in particular methyl, ethyl or n-propyl, W^4 , W^5 and W^6 being independently of each other Cl, oxalkyl or oxacarbonylalkyl with 1 to 5 C-atoms, Phe being 1,4-phenylene and k_1 and k_2 being independently of each other

0 or 1.

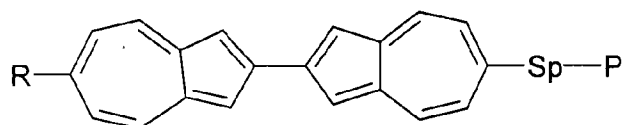
8. Reactive mesogenic azulenenes according to at least one of claims 1 to 7, **characterized in that** they are selected from the following formulae



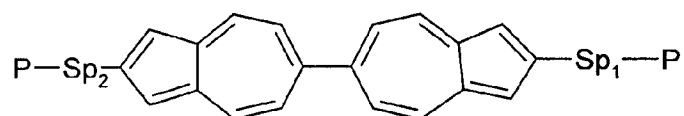
I1



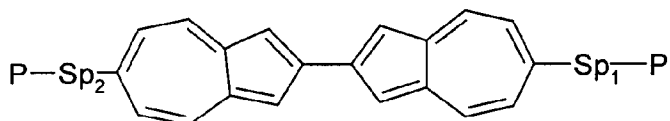
I2



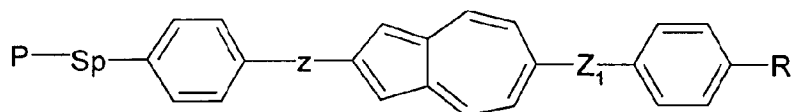
I3



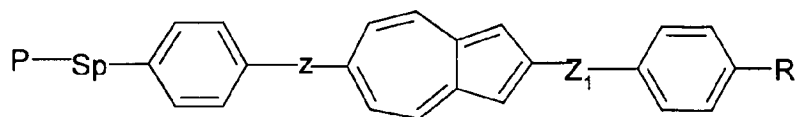
I4



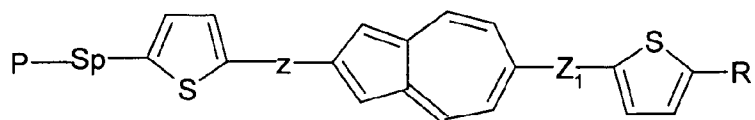
I5



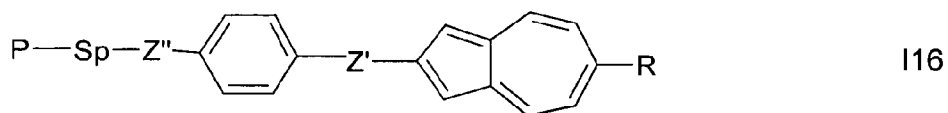
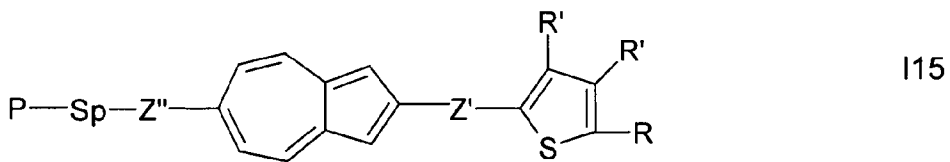
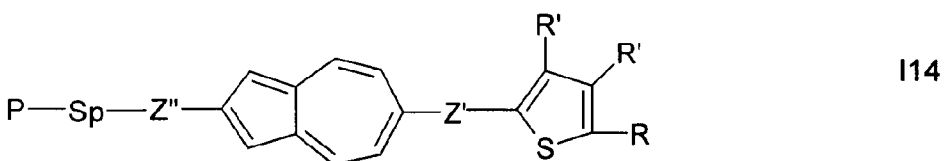
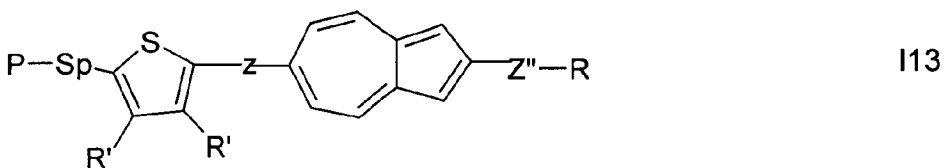
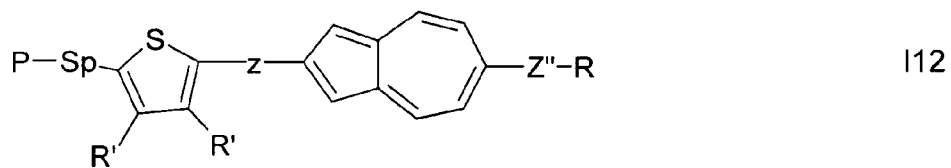
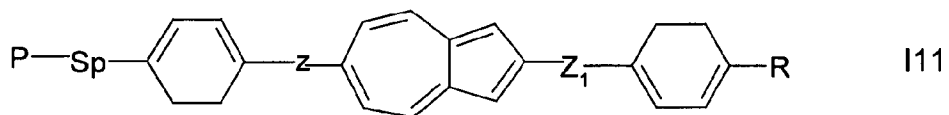
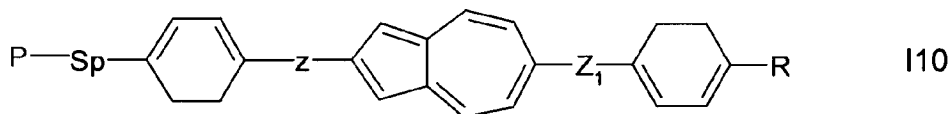
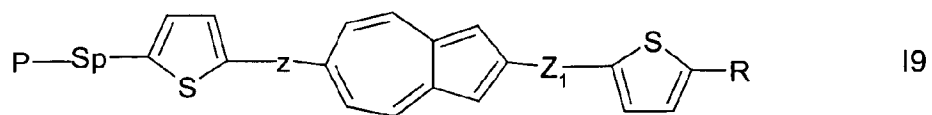
I6

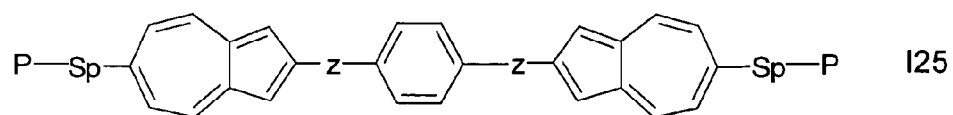
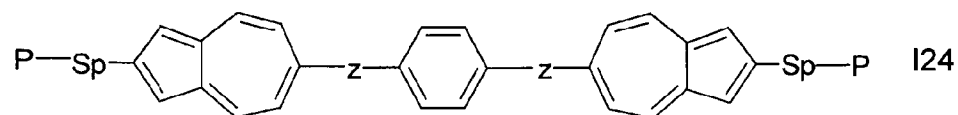
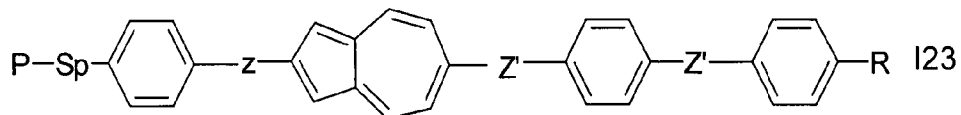
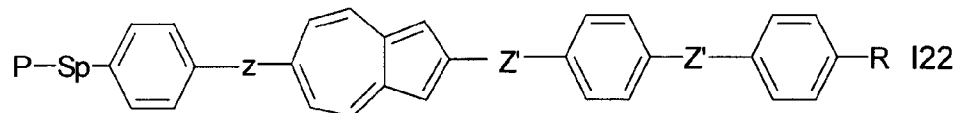
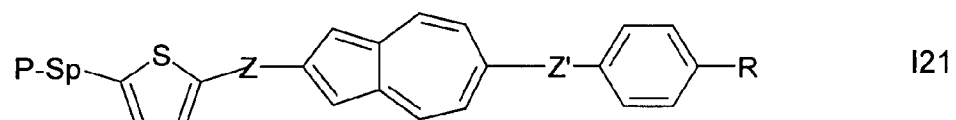
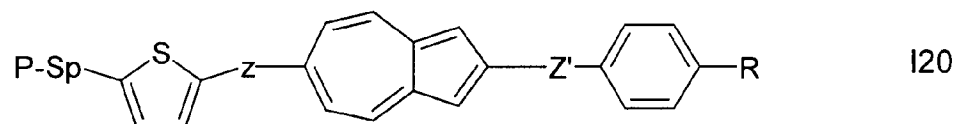
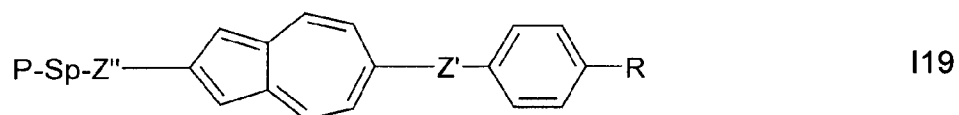
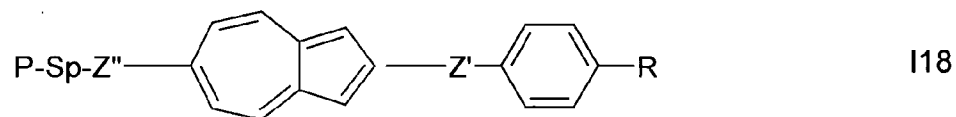
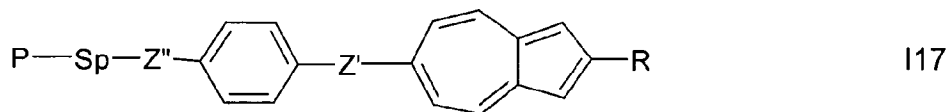


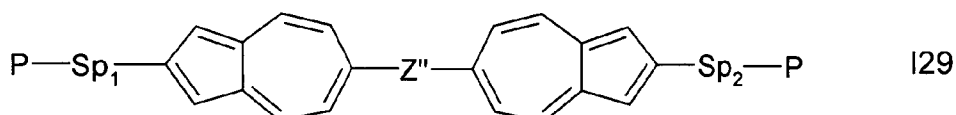
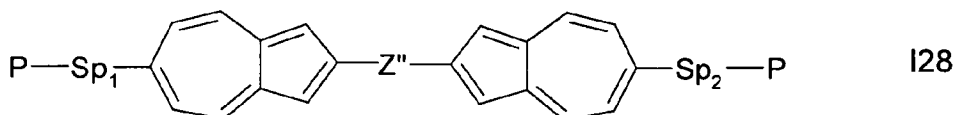
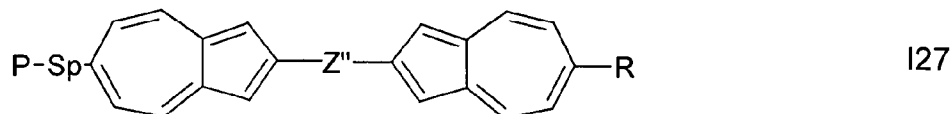
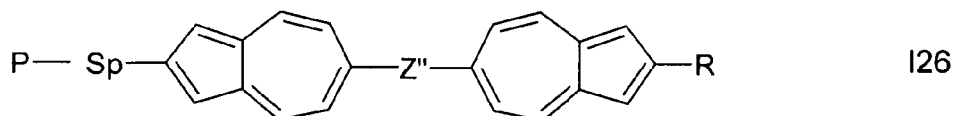
I7



I8







wherein P, Sp and n have the meanings of formula I,

30 Sp^1 and Sp^2 are different groups Sp as defined in formula I,

Z and Z' have independently of each other one of the meanings of Z^1 in formula II, and are preferably $-CH=CH-$, $-CH=CF-$, $-CF=CH-$, $CH=CCl-$, $-CCl=CH-$, $-CF=CF-$, $-CCl=CCl-$, $-C\equiv C-$ or a single bond,

35 Z'' has one of the meanings of Z^1 in formula II, and is preferably $-CH=CH-$, $-CH=CF-$, $-CF=CH-$, $CH=CCl-$, $-CCl=CH-$, $-CF=CF-$, $-CCl=CCl-$ or $-C\equiv C-$,

R has in each case independently one of the meanings of R^1 of formula I,

40 R' has in each case independently one of the meanings of R^2 of formula II,

wherein the azulene group is optionally mono- or polysubstituted by R^2 as defined in formula II, and wherein in formulae I6 to I29 the azulene-2,6-diyl groups are optionally replaced, independently in each occurrence, by [2,6']-bisazulene-6,2'-diyl, [2,2']-bisazulene-6,6'-diyl or [6,6']-bisazulene-2,2'-diyl, all of which are optionally mono- or polysubstituted by R^2 as defined in formula II.

9. Reactive mesogenic azulenes according to at least one of claims 1 to 8, **characterized in that** they are mesogenic or liquid crystalline.

50 10. Reactive liquid crystal mixture comprising one or more reactive mesogenic azulenes according to at least one of claims 1 to 9 and optionally one or more further reactive compounds, wherein at least one of said azulenes and further reactive compounds is mesogenic or liquid crystalline.

55 11. Anisotropic polymer film with charge transport properties obtainable from a reactive liquid crystal mixture according to claim 10 that is aligned in its liquid crystal phase into macroscopically uniform orientation and polymerised or crosslinked to fix the oriented state.

12. Side chain liquid crystal polymer obtained by polymerisation of one or more compounds or a polymerisable material

according to claims 1 to 10 or by grafting one or more compounds or a polymerisable material according to claims 1 to 10 to a polymer backbone in a polymeranalogous reaction, optionally with one or more additional mesogenic or non-mesogenic comonomers.

- 5 **13.** Use of the reactive mesogenic azulenes, reactive mixtures and polymers according to at least one of claims 1 to 12 as semiconductors or charge transport materials, in particular in optical, electrooptical or electronic devices, like for example components of integrated circuitry, field effect transistors (FET) for example as thin film transistors in flat panel display applications or for Radio Frequency Identification (RFID) tags, or in semiconducting components for organic light emitting diode (OLED) applications such as electroluminescent displays or backlights of e. g. liquid crystal displays, for photovoltaic or sensor devices, as electrode materials in batteries, as photoconductors and for electrophotographic applications like electrophotographic recording, or as light-modulating components for liquid crystal displays, optical films or other optical or electrooptical devices.
- 10
- 15 **14.** Field effect transistor, for example as a component of integrated circuitry, as a thin film transistor in flat panel display applications, or in a Radio Frequency Identification (RFID) tag, comprising one or more reactive mesogenic azulenes, reactive mixtures or polymers according to at least one of claims 1 to 12.
- 20 **15.** Security marking or device comprising comprising one or more reactive mesogenic azulenes, reactive mixtures or polymers according to at least one of claims 1 to 12, or a FET or RFID tag according to claim 14.
- 25 **16.** Reactive mesogenic azulenes, reactive mixtures or polymers according to at least one of claims 1 to 12, which are oxidatively or reductively doped to form conducting ionic species.
- 30 **17.** Charge injection layer, planarising layer, antistatic film or conducting substrate or pattern for electronic applications or flat panel displays, comprising one or more reactive mesogenic azulenes, reactive mixtures or polymer films according to claim 16.
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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 02 02 5130

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
D,A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 250 (C-0723), 29 May 1990 (1990-05-29) -& JP 02 069441 A (MITSUBISHI KASEI CORP), 8 March 1990 (1990-03-08) * abstract *	1-17	C09K19/32
D,A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 250 (C-0723), 29 May 1990 (1990-05-29) -& JP 02 069437 A (MITSUBISHI KASEI CORP), 8 March 1990 (1990-03-08) * abstract *	1-17	
D,A	PATENT ABSTRACTS OF JAPAN vol. 015, no. 324 (C-0859), 19 August 1991 (1991-08-19) -& JP 03 122189 A (MITSUBISHI KASEI CORP), 24 May 1991 (1991-05-24) * abstract *	1-17	
D,A	WO 97 00600 A (BASF AG) 9 January 1997 (1997-01-09) * claims *	1-3	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C09K
A	EP 0 187 015 A (MITSUBISHI CHEM IND) 9 July 1986 (1986-07-09) * claims *	1-10	
A	ESTDALE S E ET AL: "THE AZULENE RING AS A STRUCTURAL ELEMENT IN LIQUID CRYSTALS" JOURNAL OF MATERIALS CHEMISTRY, THE ROYAL SOCIETY OF CHEMISTRY, CAMBRIDGE, GB, vol. 7, no. 3, 1 March 1997 (1997-03-01), pages 391-401, XP000693112 ISSN: 0959-9428 * the whole document *	1-10	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10 March 2003	Examiner Serbetsoglou, A
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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EUROPEAN SEARCH REPORT

Application Number
EP 02 02 5130

DOCUMENTS CONSIDERED TO BE RELEVANT				
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)	
A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 250 (C-0723), 29 May 1990 (1990-05-29) -& JP 02 069439 A (MITSUBISHI KASEI CORP), 8 March 1990 (1990-03-08) * abstract *	1-10		
A	--- PATENT ABSTRACTS OF JAPAN vol. 014, no. 250 (C-0723), 29 May 1990 (1990-05-29) -& JP 02 069438 A (MITSUBISHI KASEI CORP), 8 March 1990 (1990-03-08) * abstract *	1-10		
A	--- PATENT ABSTRACTS OF JAPAN vol. 009, no. 247 (C-307), 3 October 1985 (1985-10-03) -& JP 60 104180 A (CANON KK), 8 June 1985 (1985-06-08) * abstract *	1-10		
E	--- EP 1 256 602 A (ROLIC AG) 13 November 2002 (2002-11-13) * page 5, paragraph 15; claims *	1		TECHNICAL FIELDS SEARCHED (Int.Cl.7)
A	--- US 4 738 908 A (OGUCHI YOSHIHIRO ET AL) 19 April 1988 (1988-04-19) * claims *	1		
The present search report has been drawn up for all claims				
Place of search THE HAGUE		Date of completion of the search 10 March 2003	Examiner Serbetsoglou, A	
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document		

EPO FORM 1503 03/02 (P04/C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 02 5130

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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10-03-2003

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
JP 02069441	A	08-03-1990	JP	2033133 C	19-03-1996
			JP	7068174 B	26-07-1995
JP 02069437	A	08-03-1990	JP	2028960 C	19-03-1996
			JP	7061984 B	05-07-1995
JP 03122189	A	24-05-1991	NONE		
WO 9700600	A	09-01-1997	DE	19532408 A1	06-03-1997
			DE	59607179 D1	02-08-2001
			WO	9700600 A2	09-01-1997
			EP	0847432 A2	17-06-1998
			JP	11513019 T	09-11-1999
			US	6136225 A	24-10-2000
EP 0187015	A	09-07-1986	JP	61145143 A	02-07-1986
			JP	61218550 A	29-09-1986
			JP	61218551 A	29-09-1986
			JP	61238755 A	24-10-1986
			JP	61243862 A	30-10-1986
			JP	61260038 A	18-11-1986
			JP	1985241 C	25-10-1995
			JP	7005551 B	25-01-1995
			JP	62000465 A	06-01-1987
			JP	62000432 A	06-01-1987
			JP	61145284 A	02-07-1986
			DE	3583013 D1	04-07-1991
			EP	0187015 A2	09-07-1986
			US	5037575 A	06-08-1991
JP 02069439	A	08-03-1990	JP	2033132 C	19-03-1996
			JP	7068173 B	26-07-1995
JP 02069438	A	08-03-1990	JP	2028961 C	19-03-1996
			JP	7061985 B	05-07-1995
JP 60104180	A	08-06-1985	NONE		
EP 1256602	A	13-11-2002	EP	1256602 A1	13-11-2002
			WO	02090447 A1	14-11-2002
US 4738908	A	19-04-1988	JP	1579908 C	13-09-1990
			JP	2005594 B	02-02-1990
			JP	61027293 A	06-02-1986
			JP	1579910 C	13-09-1990
			JP	2002715 B	19-01-1990

EPO FORM P/489

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 02 5130

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

10-03-2003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4738908 A	JP	61068294 A	08-04-1986
	JP	1657566 C	21-04-1992
	JP	2057030 B	03-12-1990
	JP	61108584 A	27-05-1986
	JP	1657567 C	21-04-1992
	JP	2057031 B	03-12-1990
	JP	61108590 A	27-05-1986
	JP	1576127 C	24-08-1990
	JP	2002716 B	19-01-1990
	JP	61108591 A	27-05-1986
	JP	1657568 C	21-04-1992
	JP	2057032 B	03-12-1990
	JP	61108592 A	27-05-1986
	JP	1657569 C	21-04-1992
	JP	2057033 B	03-12-1990
	JP	61108593 A	27-05-1986

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82